

Quantification of Ultra-Trace Levels of Mercury in Food and Water

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Background

- The World Health Organization considers mercury to be “one of the top ten chemicals of major public health concern” [1]
- Even ultra-trace levels of mercury in food and water can pose health risks due to the element’s high degree of toxicity, particularly during the developmental stages of life
- The accurate and precise quantification of mercury at such low levels can be very challenging, and detection limits are often higher-than-ideal due to the contribution of the blank signal and long residence time of mercury in typical instrumental setups, requiring laborious washout procedures
- Analyte losses during sample preparation are not uncommon, and must be accounted for in order to obtain accurate measurement results

Method Notes

Thermal Decomposition Atomic Absorption Spectrometry (TD-AAS)

- Direct analysis of solids, liquids, and slurries
- Absolute detection limits of 0.01 ng Hg
- Square regressions of calibration curves result in more accurate quantification (but more complicated uncertainty calculations)
- Limited to small sample sized (typically 50-150 mg), meaning samples should always be run in (at least) triplicate to account for potential inhomogeneity
- Online preconcentration is possible, but very time/labour intensive and may be limited by the blank in certain matrices
 - In these scenarios, the use of calibration curves including only low-level standards, closely matching the Hg amount in the sample, is vital

Cold-Vapour Atomic Fluorescence Spectrometry (CV-AFS)

- Water samples can be analyzed directly following the addition of BrCl (to stabilize the Hg) and filtration (if required)
- Solid samples require acid digestion (H_2SO_4 / HNO_3 / HCl) followed by stabilization with BrCl
- Detection limits of ~0.4 pg/g in solution (~80 pg/g in solids)
- For ultra-trace analysis, the thorough cleaning of glassware and use of high-purity reagents is vital

Isotope Dilution Inductively-Coupled Plasma Mass Spectrometry (ID-ICP-MS)

- Samples are spiked with an isotopically-enriched Hg standard prior to microwave-assisted acid digestion (HNO_3 / H_2O_2)
 - Ideally, this includes a pre-screening of the sample such that the spike is added to the sample in an amount to achieve a one-to-one ratio between the reference and spike isotopes
- Detection limits of ~10 pg/g in solution (1000 pg/g in solids)
- Sensitivity can be increased by coupling ICP-MS to a cold-vapour sample introduction system (but this requires low blanks from high-purity reagents)
- Higher-order isotope dilution strategies, including calibration graphs, can be employed to reduce measurement uncertainty [2,3]

Results

Ultra-Trace Mercury in Water & Development of Certified Reference Material ORMS-6

- Thorough cleaning and preparation was required prior to the production and ampouling of CRM ORMS-6
 - All steps up to and including the flame-sealing of ampoules were conducted in a Class-100 cleanroom facility
 - Any equipment to be in contact with the ORMS-6 solution was cleaned by soaking in 0.5% BrCl for at least 48 hours, then triple-rinsed with ultra-pure water
 - Ampoules were baked for at least 12 hours at 105°C
- The background Hg signal was regularly monitored to confirm a lack of contamination
- During ampouling, aliquots were checked, in real-time, at regular intervals to ensure homogeneity of the batch
- The resulting material was irradiated at ≥ 25 kGy to eliminate the potential for alteration of the material due to microbial activity
- The certified Hg content was established through the combination of CV-AAS following calibration by the method of standard additions, and ID-CV-ICP-MS (Figure 1)
 - TD-AAS with online preconcentration was used as a complimentary method and proof-of-concept

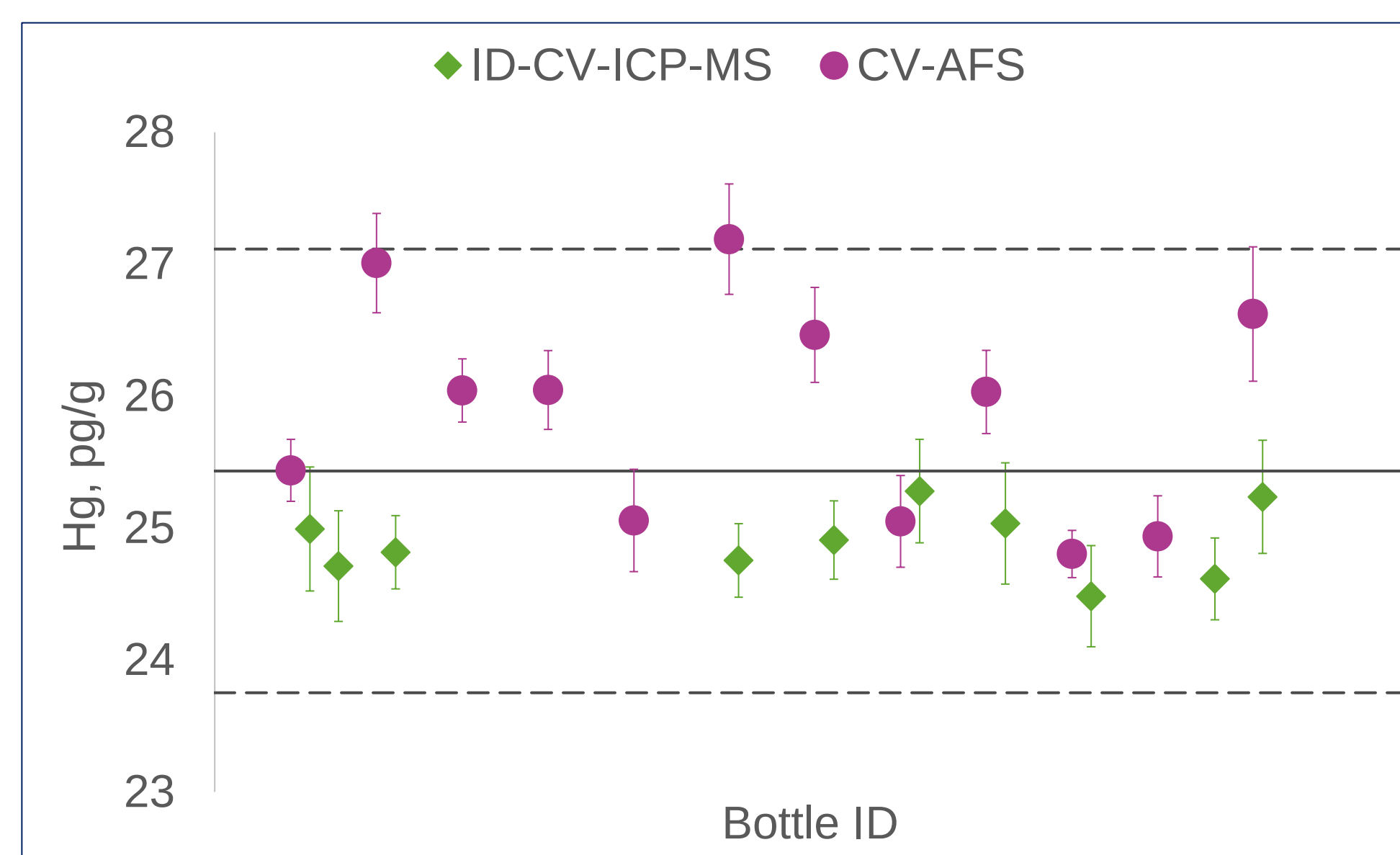


Figure 1. Mercury Content in Water CRM ORMS-6
Measured by both ID-CV-ICP-MS (green diamonds) and CV-AFS (pink circles)

Sample Preparation for Isotope Dilution

- Samples are pre-screened for their Hg content
 - TD-AAS allows this to be performed quickly
- Prior to digestion, samples are spiked to achieve a one-to-one ratio between the reference and spike isotope
- For analysis by ICP-MS, samples are digested in a batch, along with QC samples:
 - 0.25 mL sample + 7 mL HNO_3 + 0.5 mL H_2O_2
 - Microwave digestion protocol: ramp to 1500 W over 15 minutes, then hold at 1500 W for 40 minutes
- For tissue samples with very low concentrations of Hg, the digestion protocol for cold vapour generation is used (see next panel for details) following spiking with isotopically-enriched standards

Sample Preparation for Cold-Vapour Methods



Tissue samples following the modified EPA Method 1631 digestion protocol and dilution with 0.5% BrCl

- The sample digestion procedure used is based on a modification of US EPA Method 1631 [4]
 - 0.25 g sample + 7 mL H_2SO_4 + 3 mL HNO_3 + 1 mL HCl
 - Digestion allowed to proceed at 50°C for 16.5 hours (until solution becomes clear)
 - Dilution with 40 mL 0.5 % BrCl
- For calibration via the method of standard additions, the digested sample is split into three aliquots, one run unspiked and the others spiked with approximately 1-fold and 2-fold the native Hg concentration

Pushing the (Detection) Limits of TD-AAS

- Calibration solutions are diluted in 1% HCl, from the stock primary standard on the day of analysis to maximize the stability of Hg in solution
 - Multiple solutions are prepared such that a constant volume (of the blank and each calibration point) can be used to ensure a representative blank subtraction
- To ensure the accuracy of the low-level calibration, several calibration plots are prepared
 - The calibration curve used for each sample is selected based on pre-defined peak height ranges – i.e. peaks less than 0.03 units would use the left curve in Figure 2, where points fit better than in the right plot, where all calibration points were used to define the curve

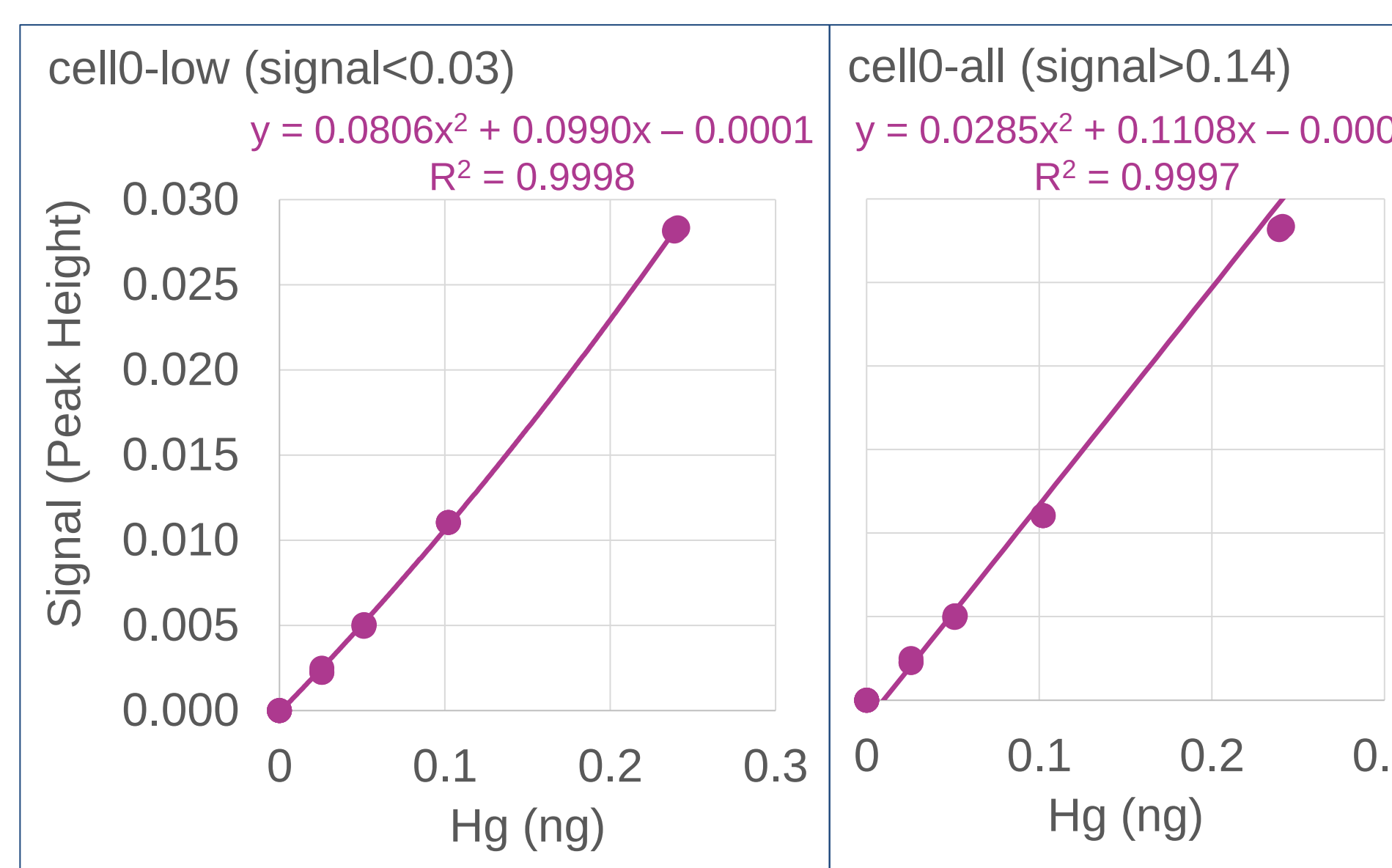


Figure 2. Low-Level Calibration for Mercury Analysis by TD-AAS. Based on absolute amount of Hg in 100 μL aliquots of standard solution, each measured in triplicate. The curve on the left uses only the lowest calibration points, while the one on the right uses all points (but is zoomed in for this figure)

Certified Reference Materials

- To support the analytical chemistry community, we are working towards assigning Hg content values to as many food / tissue CRMs as we have available
 - These will cover a wide range of Hg content (see Figure 3) as well as varying matrix compositions (i.e. high protein and/or high fat)

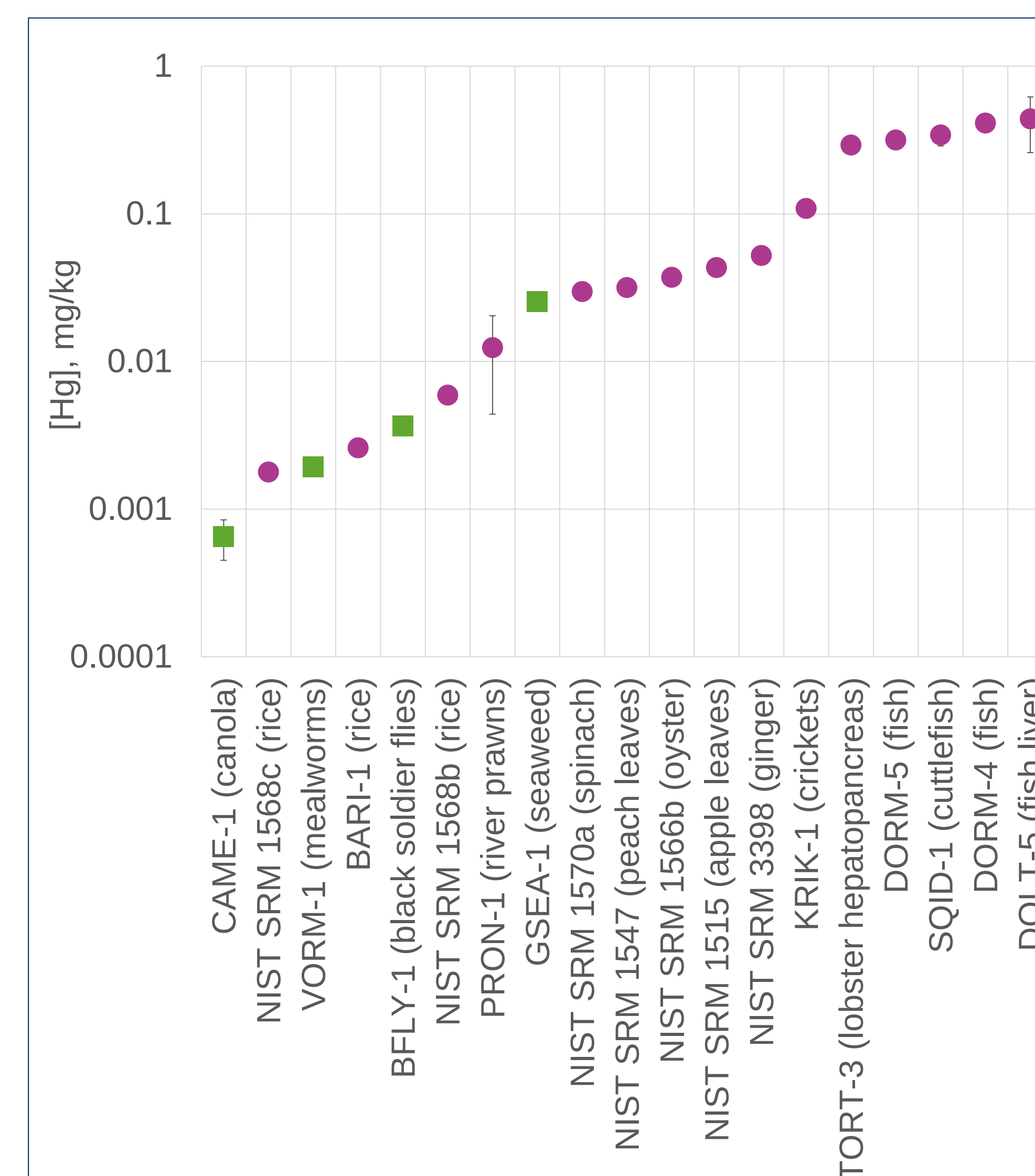


Figure 3. Mercury Content in Food / Tissue Certified Reference Materials from NRC and NIST [5,6]. Square green data points represent values which have been measured by these techniques but not yet added to the Certificates of Analysis

Conclusions

- The implementation of various protocols for sample preparation and analysis have allowed us to perform accurate and precise quantitation of the mercury content of several different types of samples, and develop associated CRMs for trace mercury content
- Our hope is that by achieving our overall goal of decreasing detection limits and improving the precision and accuracy of mercury analysis, we will move closer towards meeting regulations and targets for decreasing mercury contamination in the environment and therefore in our food

References

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